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Study of fluorine behavior in silicon by selective point defect injection

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This letter reports a point defect injection study of 185 keV 2.3×10^{15} cm^{-2} fluorine implanted silicon. After an inert anneal at 1000 °C, fluorine peaks are seen at depths of $0.3R_p$ and R_p and a shoulder between $0.5-0.7R_p$. The shallow peak (at $0.3R_p$) is significantly smaller under interstitial injection than under both inert and vacancy injection conditions. For a longer anneal under interstitial injection, both the shallow peak and the shoulder are eliminated. These results support earlier work suggesting that the shallow fluorine peak is due to vacancy-fluorine clusters which are responsible for suppression of boron thermal diffusion in silicon. The elimination of the shallow fluorine peak and the shoulder is explained by the annihilation of vacancies in the clusters with injected interstitials. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1984094]

The implantation of fluorine into silicon has already been recognized as an effective way to reduce boron transient-enhanced diffusion (TED).[1] TED, which is caused by ion implantation damage, limits the scaling of both metal-oxide-semiconductor (MOS) transistors and bipolar transistors.[2] Fluorine improves the threshold voltage roll-off characteristics in p-channel MOS transistors when introduced in the source/drain extension region[3] and also produces a super sharp halo profile in n-channel MOS transistors.[4]

The reduction of boron TED is observed when fluorine is implanted either as BF_2^+ or as a separate F$^+$ ion.[5–11] However, separate fluorine implantation allows the depth of the fluorine profile to be tailored to give the maximum diffusion suppression for a given depth of boron implant. Recently, it has been demonstrated that an optimized fluorine implant completely eliminates boron TED and also suppresses boron thermal diffusion in both subamorphized[9,10] and preamorphized substrates.[11] Such promising results have increased the need to understand the mechanism by which fluorine reduces boron diffusion.

El Mubarek *et al.*[9] who used a 185 keV 2.3×10^{15} cm^{-2} F$^+$ implant showed that the fluorine profile after anneal exhibited two distinctive peaks: A shallow peak around $R_p/2$ (between $0.3-0.5R_p$) and a deep peak at R_p. A shoulder was also observed between the shallow and deep peaks. It was demonstrated that the shallow fluorine peak was responsible for the reduction of boron thermal diffusion in silicon, and it was proposed that the reduced boron thermal diffusion was due to the formation of vacancy-fluorine clusters which created an undersaturation of the interstitial concentration in the vicinity of boron profile located around $R_p/2$ of the fluorine implant.

In this letter, we employ a point defect injection technique to study whether the shallow fluorine peak is influenced by vacancy and interstitial injection and, hence, whether it is indeed due to vacancy-fluorine clusters. The point defect injection is achieved by annealing silicon capped with a nitride layer (vacancy injection), an oxide and nitride layer (inert injection), and an uncapped layer (interstitial injection) in an oxygen atmosphere.[12]

185 keV 2.3×10^{15} cm^{-2} fluorine was implanted into a silicon epitaxial layer which was grown on a Si (100) substrate at 750 °C using low pressure chemical vapor deposition. The wafer was then divided into three parts for defect injection study as shown in Fig. 1. The first part was covered with low-temperature SiO_2 (LTO) and Si_3N_4 layers for inert anneal, the second part was covered with a Si_3N_4 layer for vacancy injection, and the last part was bare silicon for interstitial injection. This method of selective point defect injection has been successfully applied to boron and arsenic diffusion in Si and SiGe alloys.[12,13] The LTO (~100 nm) and Si_3N_4 (~130 nm) layers were deposited using chemical vapor deposition and plasma enhanced chemical vapor deposition at 400 °C and 300 °C, respectively. The wafer was then cut into 1 cm × 1 cm pieces, which were annealed at 1000 °C for 10 s, 30 s, and 180 s in an oxygen atmosphere using a rapid thermal annealer. The LTO and nitride layers were stripped before secondary ion mass spectroscopy (SIMS) analysis. Positive secondary ions were detected in the SIMS analysis, using a 10 keV 0.8 μA O_2^+ primary ion bombardment.

Figure 2 shows the fluorine profiles after annealing under different point defect injection conditions. The as-implanted profile is also shown for reference. The projected

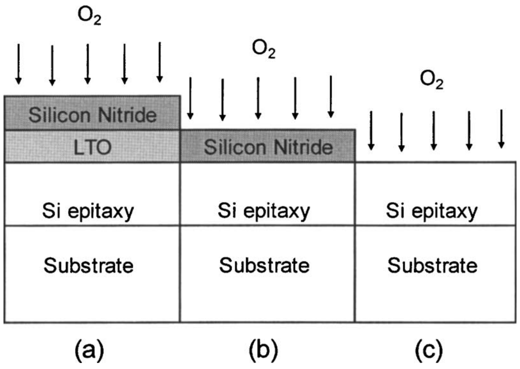

FIG. 1. Different surface layers utilized in samples for point defect injection: (a) Si_3N_4 and LTO layers for inert annealing, (b) Si_3N_4 layer for vacancy injection, and (c) bare silicon surface for interstitial injection.

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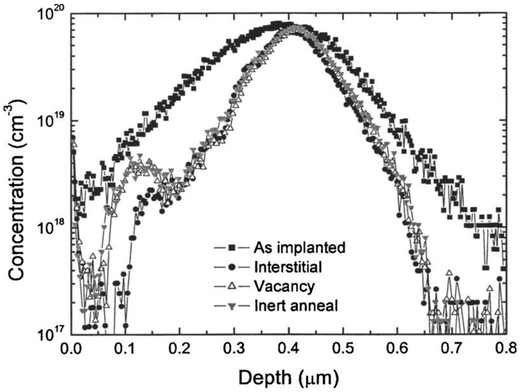

FIG. 2. Fluorine SIMS profiles after a 185 keV 2.3×10^{15} cm^{-2} F$^+$ implant and after anneal for 30 s at 1000 °C under different point defect injection (interstitial, vacancy, and inert) conditions.

range, R_p, of the fluorine implant is around 0.4 μm. The inert annealed profile shows two distinctive peaks: The deep peak occurs at a depth of 0.42 μm, which is slightly deeper than R_p and the shallow peak lies at a depth of 0.12 μm, which is at $0.3R_p$. In between, a noticeable shoulder is observed, at a depth between 0.2 and 0.28 μm. Under vacancy injection, the fluorine profile shows no obvious differences from the profile measured under inert injection. In contrast, under interstitial injection, the shallow fluorine peak is smaller than for the other two conditions and lies deeper in the silicon, appearing at a depth of 0.15 μm.

To further confirm this behavior, annealing under interstitial injection condition was carried out for different times (10 s and 180 s). Figure 3 shows the evolution of fluorine profile over time during interstitial injection. The shallow fluorine peak decreases in size as the anneal time increases and it is completely eliminated after the 180 s anneal. The shoulder, which is noticeable even after the 10 s anneal, is also eliminated after the 180 s anneal.

It is now generally agreed that following an implant, vacancies are the dominating defect species in a layer between the surface and approximately R_p, while self-interstitials are mainly observed around R_p and beyond.[14] El Mubarek *et al.*[9] proposed that the shallow fluorine peak responsible for a reduction in boron thermal diffusion was due to vacancy-fluorine clusters. The behavior of the shallow peak observed under interstitial injection in Fig. 2 tends to support the idea that it is indeed due to vacancy-fluorine clusters. The smaller peak size under interstitial injection is consistent with the annihilation of vacancy-fluorine clusters by the interstitials injected from the surface during annealing. Fluorine released from the annihilation of the vacancy-fluorine clusters will diffuse out from the surface.[8] The shift of the peak deeper into the silicon is also consistent with this explanation, since the interstitials injected from the surface would be expected to annihilate clusters lying closer to the surface before deeper clusters. The elimination of the shoulder after a 180 s anneal in Fig. 3 suggests that it is also due to vacancy-fluorine clusters.

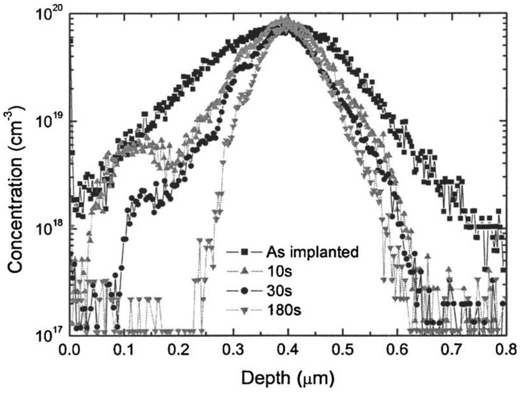

FIG. 3. Fluorine SIMS profiles after a 185 keV 2.3×10^{15} cm^{-2} F$^+$ implant and after anneal at 1000 °C for 10 s, 30 s, and 180 s under interstitial injection conditions.

These results are consistent with the work of Pi *et al.*[15] who used positron annihilation spectroscopy to study fluorine profiles, and suggested that vacancy-dominated vacancy-fluorine clusters are formed in the region of $0-0.5R_p$ and fluorine-dominated vacancy-fluorine clusters are formed in the region of $0.5R_p-1.3R_p$. In our work, the shallow fluorine peak lies between $0.2-0.5R_p$ and the shoulder lies between $0.5-0.7R_p$ (Fig. 2). These depths broadly correspond to the work of Pi *et al.*[15] and suggest that the shallow fluorine peak may be due to vacancy-rich clusters and the shoulder to fluorine-rich clusters.

While the vacancy-fluorine clusters are annihilated under interstitial injection, Fig. 2 shows that they are unchanged under vacancy injection. The vacancy injection occurs due to the compressive strain at the silicon caused by the deposited nitride layer and thus its effect is dependent on the thickness of the layer.[16] The retardation of boron diffusion by vacancy injection is not as strong as the enhancement of boron diffusion caused by interstitial injection for a given nitride thickness.[17] Further anneals with a thicker nitride layer or a longer anneal time under vacancy injection condition will be necessary to see an effect on the vacancy-fluorine clusters.

In summary, a study has been made of the effect of point defect injection on ion-implanted fluorine profiles during anneal at 1000 °C. Under inert anneal conditions, peaks are seen at depths of $0.3R_p$ and R_p and a shoulder between $0.5-0.7R_p$. Under interstitial injection anneal conditions, the shallow fluorine peak decreases in size and, for long anneal times, both the shallow peak and the shoulder are completely eliminated. This result provides strong evidence that the shallow peak and the shoulder are due to vacancy-fluorine clusters. The elimination of both the shallow fluorine peak and the shoulder can be explained by the annihilation of vacancies in the clusters by recombination with injected interstitials. It is proposed that the shallow fluorine peak is due to vacancy-rich clusters and the shoulder is due to fluorine-rich clusters.

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